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Pi-conjugated polyradicals are of interest as potential superparamagnetic species with possible uses as organic magnetic information storage materials. Experimental results to date suggest that simple parity-based qualitative models are not entirely successful in making global predictions of ground state (GS) spin multiplicity for various connecitvity classes of organic polyradicals. We show that a variety of experimentally known diradicals are well described by a semiempirical MO-CI model based on AM1, and that our semiempirical approach gives predictions in good accord with ab initio work where experiments are yet to be performed. The use of such predictive algorithms is described in making rational selection of model compounds for testing spin-magnetic interactions in organic systems.

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THEORETICAL INVESTIGATIONS OF PI-CONJUGATED POLYRADICALS
AS MODELS FOR ORGANIC MAGNETIC MATERIALS

by Paul M. Lahti[*]

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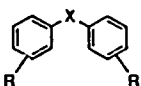
by

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INTRODUCTION:

Recent interest in synthesizing organic polyradicals with very high spin ground states has been spurred by the hope that macromolecular pi-conjugated polyradicals could have superparmagnetic or ferromagnetic properties of potential use as one of the several recently suggested types of magnetic information storage materials(1-5). Our group has been interested in synthesis of pi-conjugated model systems based upon coupling of phenoxy radicals and phenyl nitrenes by a variety of connecting spacer groups, such as the selection of groups -X- shown in Figure 1. In order to select in a rational manner the model systems most likely to lead to high spin ground state (GS) molecules, we have chosen a computational procedure based upon semiempirical molecular orbital theory with configuration interaction (MO-CI method). This procedure has proved useful for a variety of diradical systems(6) by comparison to experimentally reported GS multiplicities, and therefore was applied by us to a series of unknown diradicals to evaluate a variety of spacers -X- as moieties that could allow ferromagnetic coupling of radicals to give high spin states. In principle, our findings could then further be extended to the design of polymeric systems with incorporation of similar units.

Figure 1: Molecules Investigated by AM1-CI.

$R =$ O· or N:

-⟨▢⟩- = 2,5 CP

-⟨O▢⟩- = 2,5 furan

-⟨(H)N▢⟩- = 2,5 pyrrole

#	X	Connectivity[1]	Type[2]
1	bond	m,p'	SF
2		m,m'	
3	-CH=CH-	m,p'	F
4		m,m'	
5	-(CH=CH)₂-	m,p'	F
6		m,m'	
7	-C≡C-	m,p'	F
8		m,m'	
9	-(C≡C)₂-	m,p'	F
10		m,m'	
11	p-phenylene	m,p'	WF
12		m,m'	
13	m-phenylene	m,p'	WF
14		m,m'	
15		p,p'	
16	=C=O	m,p'	Poor
17		m,m'	
18		p,p'	
19	=C=CH₂	m,p'	SF
20		m,m'	
21		m,p'	
22	-O-	m,p'	A
23		m,m'	
24		p,p'	
25	-NH-	m,p'	A
26		m,m'	
27		p,p'	
28	2,5-CP	m,p'	*
29		m,m'	
30		p,p'	
31	2,5-furan	m,p'	*
32		m,m'	
33		p,p'	
34	2,5-pyrrole	m,p'	*
35		m,m'	
36		p,p'	

[1] Connectivity of the spin group carriers R.
[2] Type refers to F=ferromagnetic. A=antiferromagnetic. S=strong. W=weak. Poor=poor coupling ability for the spacer. * = "see text."

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COMPUTATIONAL METHODS:

In our computations, we used the AM1 hamiltonian(7) in the AMPAC program(8) to obtain diradical geometries optimized at the multiplicity appropriate to the high spin state that was likely (e.g., triplet for diradicals, quintet for dinitrenes, etc.). Unless otherwise noted, planarity was imposed on the models used, since some planarization of systems with aromatic rings seems likely under solid state conditions.

Relaxation of this constraint does not in general lead to changes in the conclusions drawn from out calculations, although the spin state of the GS is in some finely balanced cases qualitatively reversed. We expect that the highest spin state geometries should be the most delocalized and allow the most spin interaction. The geometries for each model system were then fixed, and AM1-CI computations were carried out. The lowest energy states in each spin manifold were compared for each model to assess semiquantitatively the GS multiplicity and energy gap to the next highest excited state.

RESULTS AND DISCUSSION:
    Figure 1 shows a schematic of the specific systems examined in this study. Due to space limitations, we will confine our discussion to the qualitative findings of our study rather than detailed consideration the computational results for individual systems.
   Generally, we predict that simple parity models that have previously been set forth(9-12) are obeyed. For alternant diradical cases, usually the spin multiplicity $M = N_* - N_0 + 1$.(9) The energy gaps between the high spin GS states and the next lowest multiplicity states are

Multiplicity $= N_* - N_0 + 1$

triplet (M=3)   singlet (M=1)
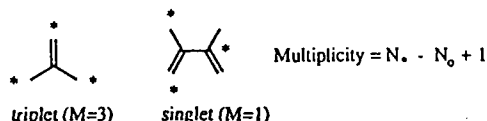
modest (2-12 kcal/mol), and depend upon the spacer -X- used in the diradical cases. Coupling is the strongest for small alternant spacers -- e.g., for R=O· cases the triplet-singlet (T-S) gap is largest for m,p'-biphenyldioxy 1. Olefinic and acetylenic spacers are predicted to be reasonably effective, even when extended to multiple units. The phenylene spacers are not found to be particularly good (giving overall 2-3 kcal/mol T-S gaps for 11 and 15) possibly due to the desire of the aromatic ring to avoid nonsextet resonance structures by isolating the spin density in separate rings that have poor spin-spin interaction through the central ring.
    When $N_* = N_0$, low spin GS's have been qualitatively predicted.(9) For many cases, we do not strictly find this to be true. However, in most such cases for $R = O^*$ the T-S gap is sufficiently small (<+1 kcal/mol) that confidence in the qualitative prediction is limited, so we feel that it is most accurate to note that small T-S gaps are found in such cases (typified by models 2, 4, 5, 8, 12, 13).
    The carbonyl spacer is found to be quite inefficient in coupling spin, with small T-S gaps and GS spin trends that do not follow the qualitative models. This appears to be due to the high bond strength of the carbonyl unit, which in ab initio work on smaller diradicals has been found to be equally ineffective at coupling radical centers to give high spin GS molecules.(13) Despite its synthetic desirability, carbonyl thus appears to be an unlikely candidate as a spacer in higher polyradicals.


carbonyl isolates   1,1-ethenediyl couples
radical centers   radical centers
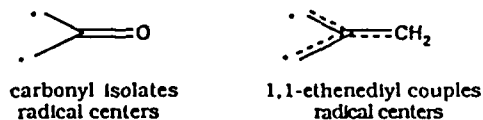
    However, the 1,1-ethenediyl spacer does seem to constitute a strong ferromagnetic coupling spacer, with R=O· T-S gaps of about 5 kcal/mol and slightly larger quintet-triplet (Q-T) gaps for R=N: in systems 20-21. Synthetic work is in progress in our labs to test these predictions.
    We also investigated the possible use of heteroatomic coupling spacers in models 22-27. Our results show that qualitative application of the GS spin multiplicity criterion given earlier is generally reversed for coupling by these one center/two electron spacers, which thus constitute antiferromagnetic coupling units. For instance, strong preferences for singlet GS's is found for p,p' cases 24 and 27 -- these species may be represented by mesoionic Kekule resonance structures,

diradical   mesoionic

rather than as diradicals. However, *m,m'* cases 23 and 26, though non-Kekule, are also found to have small gaps between high and low spin states, indicating antiferromagnetic coupling behavior. Examination of the CI wavefunctions for mesoionic *p,p'* connectivity types 24 and 27 confirms that they are not very diradicaloid. Also, *m,m'* connectivity types have CI wavefunctions indicating a highly diradical nature despite the energetically low-lying nature of these states. Again, we feel this behavior is indicative of true antiferromagnetic coupling behavior for the heteroatom spacers. We are in the process of attempting to generate diradicals and dinitrenes related to these connectivity types, in order to test experimentally our theoretical predictions.

Nonalternant spacers such as 2,5-furandiyl and 2,5-pyrrolediyl are not strictly treated by the qualitative models given before,(9-12) hence MO-CI methods such as ours constitute a most important approach to prediction of GS spin multiplicity in such cases. We investigated these spacers (Figure 1), as well as 2,5-cyclopentadienediyl, a spacer without either a pseudoaromatic sextet or a cyclic pi-system. The cyclopenta-dienediyl systems 28-29 appear to act very much like a simple diene spacers (see systems 5,6). The two pseudoaromatic systems give strong preference for singlet ground states for connectivities containing a *para*-connectivity hypovalent center (R). This is reasonable, since in systems 31, 33-34, and 36 reasonable mesoionic Kekule resonance structures may dominate the electronic structural natures, leading to low spin GS's for both of these connectivities. Where no *para* connectivity hypovalent center is available (32,33) such mesoionic structures are much less favorable, and high spin GS's result (weak ferromagnetic coupling in our results, with modest T-S and Q-T gaps). Therefore, depending on connectivity, these spacers may or may not be considered somewhat ferromagnetic or antiferromagnetic. Use of such systems in experimental polyradicals will probably require computational evaluation in individual cases for reasonably confident GS multiplicity prediction.

type 31, 34   type 33, 36
(mesoionic)   (Kekule)

type 32, 35
(diradicaloid)
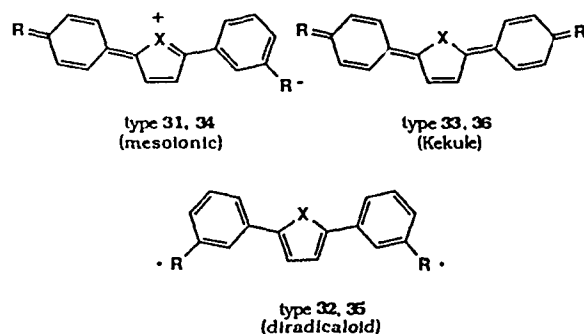
For dinitrene systems (R=N:), our qualitative results are similar to those for the dioxy diradical cases. Where $N_* > N_0$, quintet GS's are found with Q-T gaps of 2-8 kcal/mol. Qualitative trends for coupling efficiency and high spin/low spin gap parallel the findings for the diradicals. When $N_*=N_0$, the situation is somewhat different from the diradical cases, since each hypovalent site has two unpaired electrons. In these cases of predicted low spin GS multiplicity, we usually find an extremely small energy gap separating quintet and triplet states, since ferromagnetic electron pairing to give the low spin configuration in the highly spin-correlated pi-system still leaves two unpaired electrons in sigma symmetry orbitals, which turn out not to be very strongly coupled.

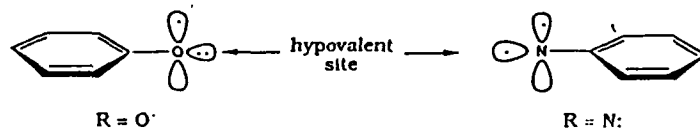R = O·   R = N:

Figure 1 summarizes our overall results, classifying the coupling units -X- investigated as ferromagnetic and antiferromagnetic, with a crude ranking of coupling strength. The rankings are based upon the size of the high spin/low spin energetic splitting in our computations, and is meant as a qualitative guide to what might be experimentally expected for coupling strength efficiency, based on our results.

For polyradical polymeric models that were optimized with AMPAC (or based upon smaller oligomeric model systems), we found that our findings could be extended to spin-spin coupling of more than two pi electrons (up to five coupled radical units). In systems 37-38 we found that high spin GS's were obtained with high spin/low spin gaps of

37   38   39
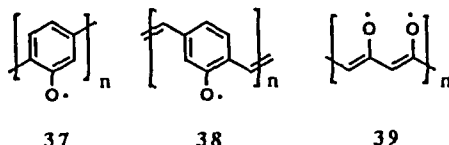
>2.5 kcal/mol for all oligomers, implying that in these unidimensional cases reasonable ferromagnetic coupling is maintained across multiple units. System 39, however, is found to possess poor coupling with gaps of <0.5 kcal/mol, suggesting that it is unlikely to be a unidimensional ferromagnet. The carbonyl containing resonance structures of 39 appear to render spin coupling inefficient, as for systems 16-18.

CONCLUSIONS:

A variety of other synthetically plausible systems is imaginable, but our results show that investigation of experimentally desirable systems may readily be carried out by our model as an aid to the selection of systems with best electronic characteristics. Relative coupling nature in differing connectivities of models with different coupling spacers may be readily compared and evaluated. Finally, a variety of electronic properties of these models may easily be extracted from computations of this sort, such as spin density distributions and interatomic bond orders.

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REFERENCES

1. Miller, J. S.; Epstein, A. J.; Reiff, W. M. Chem. Rev., 1988, 88, 201; Accts. Chem. Res., 1988, 21, 114.
2. Breslow, R. Pure Appl. Chem., 1982, 54, 927. Thomaides, J.; Maslak, P.; Breslow, R. J. Am. Chem. Soc., 1988, 110, 3970 and references therein.
3. Torrance, J. B.; Oostra, S.; Nazzal, A. Synth. Metals, 1987, 19, 709.
4. Korshak, Yu. V.; Medvedeva, T. V.; Ovchinnikov, A. A.; Spector, V. N. Nature, 1987, 126, 370.
5. Iwamura, H. Pure Appl. Chem., 1986, 58, 187.
6. Lahti, P. M.; Ichimura, A. S.; Berson, J. A. J. Org. Chem., 1989, 54, 958 and references.
7. Dewar, M. J. S.; Zoebisch, E. F.; Healy, E. F.; Stewart, J. J. P. J. Am. Chem. Soc., 1985, 107, 3902.
8. Dewar, M. J. S; Stewart, J. J. P.; et al.. QCPE 506, 1987.
9. Ovchinnikov, A. A. Theor. Chim. Acta, 1978, 47, 297.
10. Klein, D. A. Pure Appl. Chem., 1983, 55, 299.
11. Mataga, N. Theor. Chim. Acta, 1968, 10, 273.
12. Borden, W. T.; Davidson, E. R. J. Am. Chem. Soc., 1977, 99, 4587.
13. Ichimura, A. S.; Matlin, A. R.; Lahti, P. M. submitted for publication.